

IMECE2004-59357

ANALYSIS OF ENTHALPY APPROXIMATION FOR COMPRESSED LIQUID WATER

M. Kostic
 Department of Mechanical Engineering
 NORTHERN ILLINOIS UNIVERSITY
 DeKalb, IL 60115-2854, USA
 kostic@niu.edu

ABSTRACT

It is custom to approximate solid and liquid thermodynamic properties as being function of temperature only, since they are virtually incompressible, and Pdv compression work may be neglected. Furthermore, in classical literature, for isothermal compression processes, a general improvement and correction for liquid enthalpy approximation is given by adding the “pumping” work, $v\Delta P$, to the corresponding saturation value. Analysis of water real properties shows that such a correction is unnecessary for intermediate pressures and temperatures, and it is even erroneous for higher temperatures and pressures, and thus counterproductive and misleading.

NOMENCLATURE

| | |
|-------------------|---|
| c, c_p, c_v | specific heat, at constant pressure, or constant volume |
| $corr.A$ | enthalpy correction (Δu), Eq.(6) |
| $corr.B$ | enthalpy correction ($P\Delta v$), Eq.(7) |
| $corr.C$ | enthalpy correction ($v\Delta P$), Eq.(8) |
| h | liquid enthalpy at any P and T |
| h_{corr} | liquid enthalpy approximation with $v\Delta P$ correction ($corr.C$) as recommended in literature |
| h_f, h_{sat} | saturation liquid enthalpy |
| $h_{w/O}=h_{sat}$ | liquid enthalpy approximation as corresponding saturated value without any correction |
| P | pressure |
| s | entropy |
| T | temperature |
| u | internal thermal energy |
| v | specific volume |

Subscripts

| | |
|---------------|---|
| $corr$ | with $v\Delta P$ correction ($corr.C$) as recommended in literature |
| f | for saturated liquid |
| $s50$ | isentropic compression from saturated liquid state to 50 MPa |
| sat | for saturated liquid |
| $T5$ to $T50$ | isothermal compression from saturated liquid state to 5 to 50 MPa range |
| w/O | saturated liquid value without any correction |

INTRODUCTION

Since solids and liquids are virtually (but not exactly) incompressible, than the compression work, Pdv , could be neglected and thus many properties will not be function of pressure but temperature only, like specific internal energy, u , etc. Furthermore, any process is also at the same time isochoric, constant-volume process. Namely, isobaric, constant-pressure process will be simultaneously constant-volume process for incompressible substance, so that specific heat at constant pressure, c_p , and constant volume, c_v , are the same, or approximately the same for virtually incompressible real solids and fluids, particularly when compared to vapors and gases, i.e.:

$$u \approx u(T) \quad \text{and} \quad c_p \approx c_v \approx c(T) \quad (1)$$

Even the specific enthalpy for a liquid (from here on word ‘specific’ will be assumed and omitted for brevity), can be approximated to be independent from pressure and conveniently taken to be equal to the corresponding saturated liquid value at the given temperature. It is designated here as

enthalpy without (*w/O*) correction, since a correction will be presented later, i.e.:

$$h_{w/O}(P, T) \approx h_f(T) = h_{sat}(T) \quad (2)$$

However, enthalpy is unique, since it is explicitly defined as a function of pressure, namely:

$$h \equiv u + P \cdot v \quad \text{thus,} \quad h(T, P) = u(T) + P \cdot v \quad (3)$$

Therefore, it is common in all engineering references, including excellent and widely used Thermodynamics textbooks [1, 2], to evaluate change of enthalpy, assuming incompressibility ($dv=0$), but taking correction for pressure increase as:

$$dh = d(u + P \cdot v) = \underbrace{du}_{corr.A} + \underbrace{P \cdot dv}_{corr.B} + \underbrace{v \cdot dP}_{corr.C} \Big|_{dv=0} \approx du + v dP \approx cdT + v dP \quad (4)$$

Furthermore, for isothermal processes ($dT=0$ and $du \approx 0$, then $dh \approx v dP$), and finally, for finite pressure change from saturated pressure, P_{sat} , corresponding to the given temperature, T , the specific enthalpy with correction, $h_{corr}(T, P)$ at that temperature, T , and any pressure, P , will be [1,2]:

$$h_{corr}(P, T) - h_f(T) \approx \underbrace{v_f(T) \cdot (P - P_{sat})}_{\text{correction } C} \quad (5a)$$

$$h_{corr}(P, T) \approx h_f(T) + \underbrace{v_f(T) \cdot (P - P_{sat})}_{\text{correction } C} \quad (5b)$$

Where, $h_f(T)$ and $v_f(T)$ are liquid saturation enthalpy and liquid saturation specific volume at given temperature, T , respectively. It is stated in virtually all references, including [1,2], that the above equations (5a & 5b) are generally recommended as the correction for enthalpy dependence on pressure, and that it is more accurate than simple approximation without correction, $h_{w/O}$, (Eq.2).

It is objective of this paper to point out to the erroneous general recommendations in the literature The correction (Eq.5), as recommended in virtually all references, is only useful for smaller temperature and pressures, but is actually more erroneous (thus counterproductive and misleading) than

the simple approximation (Eq.2) without any correction, for larger temperatures and pressures. Illustrative examples and the corresponding analysis with physical justification are presented below.

2. ANALYSIS

Compressed liquid water properties, for different pressure at 260 °C, are presented in Table I [1]. In addition, corresponding corrections (*corr.A*, *corr.B* & *corr.C*, see Eq. 4) are tabulated along with differences of the approximated enthalpy without and with correction from the real enthalpy, in the last two columns, respectively, for saturated liquid water (f_{sat}) and compressed liquid (**T5** to **T50**), corresponding to isothermal compression from 5 to 50 MPa range. In the last row, the corresponding data are presented for isentropic (**s50**) compression to 50 MPa. Note that the tabulated enthalpy difference with correction (*corr*) is based on Eq.(5), i.e. using correction *C* only, as generally recommended in the literature, while corrections *A* & *B* are neglected [1, 2].

The corrections in Table I are calculated using Eqs.(6,7&8). It is evident from Table I, that, for the isothermal compression, the correction *B* is smaller than corrections *A* & *C* and it may be neglected. However, corrections *A* (negative) & corrections *C* (positive) are comparable in magnitude but opposite in sign, so it is better not to take them, like in Eq. (2), than to take only the correction *C*, like Eq. (5). The opposite is evident for the isentropic compression (last row in Table I).

The negative correction *A* (Δu) depends mostly on temperature, while positive correction *C* ($v \Delta P$) depends mostly on pressure. Therefore, for smaller temperatures (less than 200

$$corr.A = \Delta u = u(P, T) - u(P_{sat}, T) \quad (6)$$

$$corr.B = P \Delta v = \int P \cdot dv = \Delta h - \Delta u - \int v \cdot dP = h(P, T) - h(P_{sat}, T) - (corr.A) - (corr.C) \quad (7)$$

$$corr.C = v \Delta P = \int v \cdot dP \approx \frac{v(P, T) + v(P_{sat}, T)}{2} \cdot (P - P_{sat}) \quad (8)$$

°C) the correction, Eq. (5), cited in virtually all references, as general improvement for compressed liquid enthalpy calculation, is justified. However, it is more erroneous (and thus counterproductive and misleading) for higher temperatures (above than 200 °C) and particularly at higher pressures, so that simple approximation (Eq. 2), without any correction, is more accurate.

TABLE I: Compressed liquid water properties and relevant enthalpy corrections (*corr.A*, *corr.B* & *corr.C*, Eq.4,6-8)

| State | From Ref [1] | | | | | | <i>corr.A</i> | <i>corr.B</i> | <i>corr.C</i> | <i>w/O</i> | <i>corr</i> |
|------------|--------------|-------------|-----------------------------|----------------|----------------|------------------|-----------------------|-------------------------|-------------------------|------------------------|-------------------------|
| | P [MPa] | T [°C] | v [m ³ /kg] | u [kJ/kg] | h [kJ/kg] | s [kJ/kg·K] | Δu [kJ/kg] | $P \Delta v$ [kJ/kg] | $v \Delta P$ [kJ/kg] | $h_{sat}-h$ [kJ/kg] | $h_{corr}-h$ [kJ/kg] |
| f_{sat} | 4.688 | 260 | 0.00128 | 1128.4 | 1134.4 | 2.8838 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| T5 | 5 | 260 | 0.00127 | 1127.9 | 1134.3 | 2.8830 | -0.5 | 0.0 | 0.4 | 0.1 | 0.5 |
| T10 | 10 | 260 | 0.00126 | 1121.1 | 1133.7 | 2.8699 | -7.3 | -0.1 | 6.7 | 0.7 | 7.4 |
| T15 | 15 | 260 | 0.00126 | 1114.6 | 1133.4 | 2.8576 | -13.8 | -0.2 | 13.0 | 1.0 | 14.0 |
| T20 | 20 | 260 | 0.00125 | 1108.6 | 1133.5 | 2.8459 | -19.8 | -0.4 | 19.3 | 0.9 | 20.2 |
| T30 | 30 | 260 | 0.00123 | 1097.4 | 1134.3 | 2.8243 | -31.0 | -0.8 | 31.7 | 0.1 | 31.8 |
| T50 | 50 | 260 | 0.00120 | 1078.1 | 1138.2 | 2.7860 | -50.3 | -2.1 | 56.2 | -3.8 | 52.3 |
| s50 | 50 | 272 | 0.00123 | 1128.6 | 1189.8 | 2.8838 | 0.2 | -1.4 | 56.7 | -55.5 | 1.2 |

On Fig. 1, the compression of saturated liquid water, state (f_{sat}) at 260°C , is presented for isothermal compression to state ($T50$) at 50 MPa , and for isentropic compression to state ($s50$) to the same pressure of 50 MPa (see Table I for property data). Since $\Delta u = q + w_{comp}$ (where $dw_{comp} = Pdv$), and real liquids (in this case water) are not exactly incompressible, then during isentropic compression there will be some work (Pdv) and increase of internal energy and temperature (in this case for 12°C , from 260°C to 272°C , see last row in Table I). However, during the isothermal compression, there must be some heat transfer out, q , to cool and maintain constant water temperature, and in the process the internal energy will be decreased (see *corr.A* column in Table I). This correction is neglected in Eq. (5) even though its magnitude may be, and sometimes is, larger than the included *corr.C*. Therefore, the recommended enthalpy correction for isothermal compression in the literature is more appropriate for the isentropic than for isothermal processes, due to erroneous assumption that internal energy is not, and enthalpy is, dependent on pressure. It is exactly opposite in Table I, see how the corresponding values (u & h) change with pressure at constant temperature of 260°C .

Compressed liquid water enthalpies (h), their approximation differences ($h_{sat}-h$ and $h_{corr}-h$) and the corresponding error percentages, using saturation value (Eq.2) without any correction and the correction recommended in the literature (Eq.5), are presented in Table II, for different temperatures and pressures. The corrections, as recommended in virtually all references (Eq.5), are only useful for smaller temperature and pressures, they are about the same for intermediate pressure and temperature values (thus not necessary), but they are actually more erroneous (thus counterproductive and misleading) than the simple approximation without any correction (Eq.2), for higher temperatures and pressures, as seen from Table II.

CONCLUSION

An analysis with physical justification, supported by water real enthalpy data, regarding liquid enthalpy approximation, is presented here. The conclusion is drawn that recommendations in the literature for improvement of enthalpy calculation of compressed liquids, by accounting for pressure dependence, is not generally valid. The literature recommendations may be erroneous and thus counterproductive and misleading, as is the case for liquid water at higher temperatures and pressures. For intermediate pressures and temperatures, the enthalpy corrections recommended in the literature are unnecessary, since the errors are about the same in magnitude (but opposite in sign) as if the corresponding saturated enthalpy values without any corrections were used. The corrections are only useful for smaller temperatures and pressures. These facts are brought here to the attention of professional community, since the existing general literature recommendations and justifications may be erroneous, misleading, or not necessary.

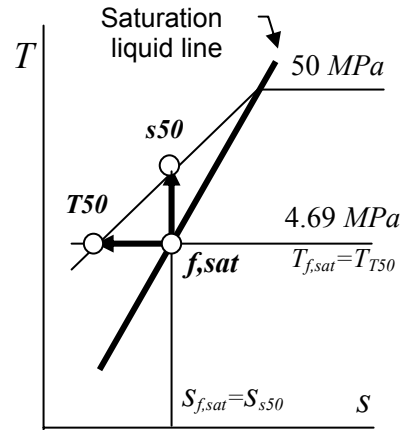


Figure 1: Isothermal and isentropic compression of saturated liquid water

TABLE II: Compressed liquid water enthalpies (h), their approximation differences ($h_{sat}-h$ and $h_{corr}-h$) and percentages, using saturation value (Eq.2) and correction recommended in the literature (Eq.5)

| $T[^\circ\text{C}]$ | 100 | | 160 | | 260 | | 360 | |
|---------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|---------------------------------|-------------------------|
| | h [kJ/kg] | | h [kJ/kg] | | h [kJ/kg] | | h [kJ/kg] | |
| P [MPa] | $h_{sat}-h$ [kJ/kg] | $h_{corr}-h$ [kJ/kg] | $h_{sat}-h$ [kJ/kg] | $h_{corr}-h$ [kJ/kg] | $h_{sat}-h$ [kJ/kg] | $h_{corr}-h$ [kJ/kg] | $h_{sat}-h$ [kJ/kg] | $h_{corr}-h$ [kJ/kg] |
| | % | % | % | % | % | % | % | % |
| Sat. | 419.04 | | 675.55 | | 1134.37 | | 1760.50 | |
| or f | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 422.72 | | 678.12 | | 1134.30 | | Water is not in liquid form. | |
| | -3.68 | 1.43 | -2.57 | 2.25 | 0.07 | 0.47 | | |
| | -0.9% | 0.3% | -0.4% | 0.3% | 0.01% | 0.04% | | |
| 10 | 426.50 | | 681.08 | | 1133.70 | | | |
| | -7.46 | 2.85 | -5.53 | 4.78 | 0.67 | 7.42 | | |
| | -1.7% | 0.7% | -0.8% | 0.7% | 0.1% | 0.7% | | |
| 15 | 430.28 | | 684.09 | | 1133.40 | | | |
| | -11.24 | 4.26 | -8.54 | 7.24 | 0.97 | 14.02 | | |
| | -2.6% | 1.0% | -1.2% | 1.1% | 0.1% | 1.2% | | |
| 20 | 434.06 | | 687.12 | | 1133.50 | | | |
| | -15.02 | 5.65 | -11.57 | 9.66 | 0.87 | 20.18 | 21.20 | 23.71 |
| | -3.5% | 1.3% | -1.7% | 1.4% | 0.1% | 1.8% | 1.2% | 1.4% |
| 30 | 441.66 | | 693.28 | | 1134.30 | | 1675.40 | |
| | -22.62 | 8.37 | -17.73 | 14.36 | 0.07 | 31.79 | 85.10 | 105.07 |
| | -5.1% | 1.9% | -2.6% | 2.1% | 0.0% | 2.8% | 5.1% | 6.3% |
| 50 | 456.89 | | 705.92 | | 1138.20 | | 1630.20 | |
| | -37.85 | 13.65 | -30.37 | 23.27 | -3.83 | 52.34 | 130.30 | 183.23 |
| | -8.3% | 3.0% | -4.3% | 3.3% | -0.3% | 4.6% | 8.0% | 11.2% |

NOTE: Liquid water enthalpy approximations with corrections, generally recommended in the literature, are more in error for higher temperature and pressure than the corresponding saturated values (see shaded values above), and are about the same for the intermediate values (e.g., 160°C).

REFERENCES

1. Cengel, Y.A., Boles, M.A., 2002, *Thermodynamics, An Engineering Approach*, 4th Edition, McGraw-Hill.
2. Moran, M.J., Shapiro, H.N., 2000, *Fundamentals of Engineering Thermodynamics*, 4th Edition, Wiley.